

UNITED STATES PATENT APPLICATION

FOR

SILICONE RUBBER COMPOSITION FOR  
APPLICATION AS ELECTRICAL INSULATION

for which the following is a specification.

BACKGROUND OF INVENTION

This invention is silicone rubber compositions for application as electrical insulation (referred to below as EI silicone rubber compositions). More specifically, this invention relates to an EI silicone rubber composition that is particularly well adapted for application as electrical insulation because after its cure it exhibits an excellent water resistance and also excellent electrical properties, for example, volume resistivity, dielectric constant, dissipation factor, tracking resistance, arc resistance, and erosion resistance.

Compositions made by blending aluminum hydroxide powder into silicone rubber compositions are already known. It is also known that silicone rubbers with excellent electrical properties can be obtained by the cure of silicone rubber compositions of this type (Japanese Patent Publication Kokoku Number Hei 5-12805 (12,805/1993) and Japanese Patent Application Kokai Number Hei 7-57574 (57,574/1995)). However, these silicone rubber compositions contain large amounts of the aluminum hydroxide powder, which is a strongly water absorptive hydrate, and as a

result have poor water resistance. These compositions absorb moisture with the passage of time, leading to a decline in their electrical insulating properties, and hence are not fully acceptable as an EI silicone rubber composition for high-voltage use.

The present invention was achieved as a result of extensive research by the present inventors directed to solving the problems described above. In specific terms, the object of the present invention is to provide a silicone rubber composition that cures into a highly water-resistant silicone rubber that has excellent electrical properties.

#### SUMMARY OF INVENTION

A silicone rubber composition for application as electrical insulation that cures into a highly water-resistant silicone rubber that has excellent electrical properties and in particular has excellent high-voltage electrical insulation properties. The silicone rubber composition comprises

- (A) polyorganosiloxane,
- (B) surface-treated aluminum hydroxide powder surface treated with an organosilane or organosilazane,
- and
- (C) curing agent.

Also, the composition afforded by the addition of 1 to 200 weight parts (D) microparticulate silica to components (A) to (C).

DESCRIPTION OF INVENTION

The present invention is an EI silicone rubber composition comprising

- (A) 100 weight parts polyorganosiloxane comprising at least 2  
5 silicon-bonded alkenyl groups in each molecule and having  
average compositional formula

$$R_aSiO_{(4 - a)/2}$$

where R is selected from substituted and unsubstituted  
monovalent hydrocarbon groups and a has a value from 1.95 to  
10 2.05,

- (B) 1 to 300 weight parts surface-treated aluminum hydroxide  
powder surface treated with an organosilane or  
organosilazane,

and

- (C) curing agent in a quantity sufficient to cure the  
15 composition.

The present EI silicone rubber composition can further  
comprise (D) 1 to 200 weight parts microparticulate silica.

To explain the preceding in greater detail, the  
20 polyorganosiloxane (A), which is the base ingredient of the  
present composition is described by the average compositional  
formula  $R_aSiO_{(4 - a)/2}$ . R in this formula is selected from  
substituted and unsubstituted monovalent hydrocarbon groups and  
is exemplified by alkyl groups such as methyl, ethyl, and propyl;  
25 alkenyl groups such as vinyl, allyl, butenyl, and hexenyl; aryl

groups such as phenyl; as well as 3,3,3-trifluoropropyl, 2-phenylethyl, and 2-cyanoethyl. Methyl preferably makes up at least 50 mole% of the R groups. The subscript a in the formula can have a value from 1.95 to 2.05. Moreover, component (A) contains at least 2 silicon-bonded alkenyl groups in each molecule. The alkenyl can be bonded in terminal or non-terminal positions or at both positions. The molecular structure of component (A) can be straight chain or partially branched straight chain. The viscosity of component (A) is not critical, but a viscosity at 25°C of from 100 mPa·s to 20,000,000 mPa·s is preferred. Component (A) may be a homopolymer or copolymer or a mixture of such polymers. The units constituting component (A) are exemplified by the dimethylsiloxyl, vinylmethylsiloxyl, methylphenylsiloxyl, and (3,3,3-trifluoropropyl)methylsiloxyl units. The endblocking groups for component (A) are exemplified by trimethylsiloxyl, silanol, vinyltrimethylsiloxyl, and vinylmethylhydroxysiloxyl. The instant polyorganosiloxane is exemplified by vinyltrimethylsiloxyl-endblocked dimethylsiloxane-vinylmethylsiloxane copolymers, vinyltrimethylsiloxyl-endblocked polydimethylsiloxanes, silanol-endblocked dimethylsiloxane-vinylmethylsiloxane copolymers, vinylmethylhydroxysiloxyl-endblocked dimethylsiloxane-vinylmethylsiloxane copolymers, and vinyltrimethylsiloxyl-endblocked dimethylsiloxane-methylphenylsiloxane-vinylmethylsiloxane copolymers.

The surface-treated aluminum hydroxide powder (B) used in the present composition has its surface treated with an

organosilane or organosilazane and is the essential component for providing the silicone rubber afforded by cure of the present composition with excellent water resistance and excellent electrical properties. The aluminum hydroxide powder comprising component (B) has a particle size preferably from 0.1 to 100  $\mu\text{m}$  and more preferably from 0.1 to 50  $\mu\text{m}$ . The organosilane which can be used as a treating agent for component (B) is exemplified by methyltrimethoxysilane, methyltriethoxysilane, phenyltrimethoxysilane, ethyltrimethoxysilane, n-propyltrimethoxysilane, vinyltrimethoxysilane, allyltrimethoxysilane, butenyltrimethoxysilane, hexenyltrimethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, diphenyldimethoxysilane, tetraethoxysilane, and the partial hydrolyzates of the preceding. The organosilazane which can be used as a treating agent for component (B) is exemplified by hexamethyldisilazane and divinyltetramethyldisilazane.

Component (B) can be prepared by treating the surface of the aluminum hydroxide powder with the organosilane or organosilazane described above by adding the aluminum hydroxide powder and organosilane or organosilazane to a mixer and blending. The treatment temperature during this procedure is preferably from 50°C to 200°C and more preferably from 80°C to 180°C. This preparation can also be carried out during production of the silicone rubber base compound by adding the aluminum hydroxide powder and organosilane or organosilazane to component (A) and

mixing while heating. The ratio of the organosilane or organosilazane to the aluminum hydroxide powder during preparation is preferably from 0.1 to 30 weight%. Component (B) is added to the present composition at from 1 to 300 weight parts and preferably at from 30 to 200 weight parts, in each case per 100 weight parts component (A). The addition of less than 30 weight parts component (B) leads to inadequate results in terms of electrical properties, such as tracking resistance and arc resistance. The addition of more than 200 weight parts component (B) leads to a substantial embrittlement of the cured product and prevents the achievement of good rubber properties.

The curing agent (C) used in the present composition cures the composition. Organoperoxides are a typical example of this component and are exemplified by benzoyl peroxide, tert-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide, dicumyl peroxide, and 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane.

Another example of the curing agent (C) is the combination of a hydrosilylation reaction catalyst and polyorganohydrogensiloxane comprising at least 3 silicon-bonded hydrogen atoms in each molecule. The polyorganohydrogensiloxane is a crosslinker component. In this case, the present composition undergoes crosslinking and curing as a result of the addition reaction of the silicon-bonded hydrogen in the polyorganohydrogensiloxane to the silicon-bonded alkenyl in component (A) in the presence of the hydrosilylation reaction catalyst. The polyorganohydrogensiloxane must contain at least 3

silicon-bonded hydrogen atoms in each molecule. The non-hydrogen silicon-bonded organic groups in the polyorganohydrogensiloxane are exemplified by alkyl groups such as methyl, ethyl, and propyl; aryl groups such as phenyl and tolyl; and substituted alkyl groups such as 3,3,3-trifluoropropyl and 3-chloropropyl.

This polyorganohydrogensiloxane can have a straight-chain, branch-containing straight-chain, cyclic, or network molecular structure. While its viscosity is not critical, its viscosity at 25°C is preferably from 3 mPa·s to 10,000 mPa·s. This component is added in a quantity that provides a value from 0.5 : 1 to 20 : 1 and preferably from 1 : 1 to 3 : 1 for the ratio of the number of moles of silicon-bonded hydrogen in the composition to the number of moles of silicon-bonded alkenyl in the composition. The present composition will not undergo an acceptable cure when this molar ratio has a value below 0.5. A value in excess of 20 can cause the production of gaseous hydrogen and foaming.

The hydrosilylation reaction catalyst used in combination with the above-described polyorganohydrogensiloxane is a cure-accelerating catalyst. Preferred among such catalysts are platinum metal, platinum compounds, and compositions whose principal component is a platinum compound, in each case insofar as the particular species manifests a catalytic activity that accelerates the hydrosilylation reaction. The platinum catalysts are exemplified by chloroplatinic acid, alcohol-modified chloroplatinic acid, platinum/diketone complexes, platinum/olefin complexes, chloroplatinic acid/alkenylsiloxane complexes, and

these species supported on a carrier such as alumina or carbon black. This component is added in a catalytic quantity, generally at from 1 to 150 weight parts and preferably at from 5 to 100 weight parts, in each case as platinum metal for each 1,000,000 weight parts component (A).

The microparticulate silica (D) which may be used in the present composition is a reinforcing filler. This component is added when higher levels of mechanical strength are required of the silicone rubber afforded by the cure of the present composition. The microparticulate silica (D) is exemplified by reinforcing silica micropowders such as dry-process silicas, for example, fumed silica, and wet-process silicas, for example, precipitated silica, and by semi-reinforcing silica micropowders such as quartz powder and diatomaceous earth. Preferred for this component are silica micropowders with a particle size  $\leq 50 \mu\text{m}$  and a specific surface area of  $\geq 50 \text{ m}^2/\text{g}$ . Even more preferred are silica micropowders of this type whose surfaces have been hydrophobicized by treatment with an organosilicon compound such as an organosilane, organosilazane, or organosiloxane oligomer. High mechanical strength of the cured composition is not achieved when too little of component (D) is added and a loss of fluidity occurs when too much is added. As a result, component (D) should be added at from 1 to 200 weight parts and preferably at from 1 to 60 weight parts, in each case per 100 weight parts component (A). When component (D) is added, the total addition of components (B) and (D) is preferably from 30 to 300 weight parts



per 100 weight parts component (A).

While the present composition comprises the above-described components (A), (B), and (C) or (A), (B), (C), and (D), insofar as the object of the present invention is not impaired the composition may also contain those additives heretofore known for use with silicone rubber compositions, for example, non-reinforcing fillers, pigments, heat stabilizers, flame retardants, internal release agents, and surface-treatment agents. The non-reinforcing fillers are exemplified by diatomaceous earth, quartz powder, mica, aluminum oxide, and titanium oxide. The pigments are exemplified by carbon black and iron oxide red, while the heat stabilizers are exemplified by rare earth oxides, rare earth hydroxides, cerium silanolates, and the cerium salts of fatty acids.

The present composition can be prepared simply by mixing the above-described components (A), (B), and (C) or components (A), (B), (C), and (D) to homogeneity. The components can be mixed using those mixing means heretofore known for use with the usual silicone rubber compositions, for example, kneader mixers, twin-screw continuous compounding extruders, and two-roll mills.

When an organoperoxide is used as the curing agent, the present composition can be cured by heating to a temperature at or above the decomposition temperature of the organoperoxide, for example, 130°C to 200°C. When, on the other hand, the combination of a hydrosilylation reaction catalyst and polyorganohydrogensiloxane has been used, the composition can be

cured by heating to 70°C to 200°C. The method for molding the present silicone rubber composition should be selected according to the particular purpose from the heretofore known molding methods, such as compression molding and extrusion molding.

5           The present composition as described above cures into highly water-resistant products that evidence low water absorption and excellent electrical properties. These products have particularly good high-voltage electrical insulating properties. Thus, the instant silicone rubber composition is well suited for  
10 use in applications that require such properties, for example, for the preparation of silicone rubber electrical insulation for outdoor use.

          The invention is explained below through working examples, in which "parts" means "weight parts" and the values reported for viscosity were measured at 25°C. The electrical properties were  
15 measured in the examples using the following methods.

          Measurement of the electrical properties of the silicone rubber composition was performed on samples press-vulcanized for 10 minutes at 170°C to mold a 2 mm-thick silicone rubber sheet.  
20 The volume resistivity, dielectric constant, and dissipation factor were measured by the methods provided in JIS C 2123, "Test Methods for Silicone Rubber Compounds". The volume resistivity was measured using a high resistance meter (High Resistance Meter 4339A from the Hewlett-Packard Company) and the dielectric  
25 constant and dissipation factor were measured using an automatic instrument for loss measurement in dielectrics (TR-1100 Model

Automatic Loss Measurement Instrument for Dielectrics from Andoh  
Denki Kabushiki Kaisha, 110 Hz).

The anti-tracking test was run in accordance with the method  
stipulated in IEC Publication 587 using a model HAT-520 from  
Hitachi Kasei Kogyo Kabushiki Kaisha. The test voltage was 3.5  
kV. The evaluation A referenced in the tables refers to the time  
required until the current flowing in a high-voltage circuit  
passing through the test specimen exceeded 60 mA. The evaluation  
B referenced in the tables refers to the time for tracking to  
reach a mark placed on the surface of the test specimen at a  
position 25 mm from the lower electrode.

Measurement of the water resistance of the silicone rubber  
composition was made on samples press-vulcanized for 10 minutes  
at 170°C to mold a 2 mm-thick silicone rubber sheet. This sheet  
was dipped in de-ionized water at room temperature for 100 hours  
and then withdrawn and the electrical properties were measured on  
the resulting sample. The <sup>percent</sup> water absorption was also measured  
from the weight change in the sheet as determined from its weight  
pre- and post-immersion.

Example 1. A silicone rubber base compound was prepared by  
combining the following and mixing to homogeneity in a kneader  
mixer: 100 parts vinyltrimethoxysiloxane-endblocked  
dimethylsiloxane-vinylmethoxysiloxane copolymer gum containing  
99.87 mole% dimethylsiloxane units and 0.13 mole% vinylmethoxysiloxane  
units and 160 parts aluminum hydroxide powder whose surface had  
been treated with vinyltrimethoxysilane (brand name: Higilite

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H42STV from Showa Denko Kabushiki Kaisha, average particle size = 1  $\mu$ m). 0.8 Part of a 50 weight% silicone oil paste masterbatch of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (curing agent) was mixed to homogeneity on a two-roll mill into 100 parts of the above-described silicone rubber base to give a curable EI silicone rubber composition. This silicone rubber composition was press-vulcanized for 10 minutes at 170°C to mold a 2 mm-thick silicone rubber sheet, on which the electrical properties and water resistance were measured. These measurement results are reported in Table 1.

Example 2. A silicone rubber base compound was prepared by combining the following and mixing to homogeneity in a kneader mixer: 100 parts vinyltrimethylsiloxy-terminated dimethylsiloxane-vinylmethylsiloxane copolymer gum containing 99.87 mole% dimethylsiloxy units and 0.13 mole% vinylmethylsiloxy units and 160 parts aluminum hydroxide powder whose surface had been treated with  $\gamma$ -methacryloxypropyltrimethoxysilane (brand name: Higelite H320ST from Showa Denko Kabushiki Kaisha, average particle size = 8  $\mu$ m). 0.8 Part of a 50 weight% silicone oil paste masterbatch of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (curing agent) was mixed to homogeneity on a two-roll mill into 100 parts of the above-described silicone rubber base to give a curable EI silicone rubber composition. This silicone rubber composition was press-vulcanized for 10 minutes at 170°C to mold a 2 mm-thick silicone rubber sheet, on which the electrical properties and water resistance were measured. These results are

reported in Table 1.

The values reported in Table 1 for the electrical properties and water resistance of the silicone rubber composition prepared as described above were measured as in Example 1.

5 Comparative example 1. A silicone rubber composition was prepared as in Example 1, but in this case using an untreated aluminum hydroxide powder (brand name: Higilite H42M from Showa Denko Kabushiki Kaisha, average particle size = 1  $\mu$ m) in place of the vinyltrimethoxysilane-treated aluminum hydroxide powder  
10 (brand name: Higilite H42STV from Showa Denko Kabushiki Kaisha, average particle size = 1  $\mu$ m) that was used in Example 1.

The properties of this silicone rubber composition were measured as in Example 1 and the obtained results are reported in Table 1.

15 Example 3. The following were mixed to homogeneity in a kneader mixer into 100 parts vinyl dimethylsiloxyl-terminated dimethylsiloxane-vinyl methylsiloxane copolymer gum containing 99.87 mole% dimethylsiloxyl units and 0.13 mole% vinyl methylsiloxyl units: 30 parts surface-treated fumed silica with a specific  
20 surface area of 120 m<sup>2</sup>/g (Aerosil R972 from Nippon Aerosil Kabushiki Kaisha) and 3 parts silanol-terminated polydimethylsiloxane with a viscosity of 30 mPa·s. This was followed by the addition of 160 parts aluminum hydroxide powder (surface pre-treated with methyltrimethoxysilane) with mixing at  
25 room temperature. The addition to 100 parts of this base of curing agent as described in Example 1 afforded a curable

silicone rubber composition. The methyltrimethoxysilane-treated aluminum hydroxide powder used in this case had been prepared by adding 1 part methyltrimethoxysilane to 100 parts of an untreated aluminum hydroxide powder (brand name: Higilite H42M from Showa Denko Kabushiki Kaisha) and mixing in a mixer for 3 hours at 120°C.

The electrical properties and water resistance of the silicone rubber composition were measured as in Example 1, and the obtained results are reported in Table 2.

Comparative example 2. The following were mixed to homogeneity in a kneader mixer into 100 parts vinyltrimethoxysilane-terminated dimethylsiloxane-vinylmethylsiloxane copolymer gum containing 99.87 mole% dimethylsiloxane units and 0.13 mole% vinylmethylsiloxane units: 30 weight parts fumed silica with a specific surface area of 200 m<sup>2</sup>/g and 12 parts silanol-terminated polydimethylsiloxane with a viscosity of 30 mPa·s as surface-treatment agent. Heating at 175°C for 30 minutes then gave a silicone rubber base. 160 Parts untreated aluminum hydroxide powder (brand name: Higilite H42M from Showa Denko Kabushiki Kaisha, average particle size = 1 μm) were then mixed to homogeneity at room temperature into the above-described silicone rubber base. The addition to 100 parts of this silicone rubber base of curing agent as described in Example 1 then afforded a curable EI silicone rubber composition. The electrical properties and water resistance of this silicone rubber composition were measured as in Example 1 and the obtained

results are reported in Table 2.

Example 4. The following were mixed to homogeneity into 100 parts vinyltrimethylsiloxy-endblocked polydimethylsiloxane with a viscosity of 10,000 mPa·s (silicon-bonded vinyl content = 0.14 weight%): 30 parts fumed silica with a specific surface area of 200 m<sup>2</sup>/g, 150 parts untreated aluminum hydroxide powder (Higilite H42M, from Showa Denko Kabushiki Kaisha), and, as surface-treatment agent, 10 parts hexamethyldisilazane and 3 parts water. This was followed by mixing for an additional 2 hours at 170°C in a vacuum to give a silicone rubber base compound. A curable EI silicone rubber composition was then prepared by mixing this base compound to homogeneity with 1.4 parts trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymer with a silicon-bonded hydrogen content of 0.7 weight% and, as hydrosilylation reaction catalyst, sufficient 3 weight% isopropanolic chloroplatinic acid solution to provide 10 ppm platinum metal. The electrical properties and water resistance of the cured EI silicone rubber composition were measured as in Example 1, and these results are reported in Table 3.

Table 1

	Example 1	Example 2	Comparative Example 1
<u>initial</u>			
volume resistivity ( $\Omega$ -cm)	$1.2 \times 10^{14}$	$1.5 \times 10^{14}$	$1.9 \times 10^{14}$
dielectric constant	4.4	4.0	4.0
dissipation factor	$1.4 \times 10^{-2}$	$9.0 \times 10^{-3}$	$1.2 \times 10^{-2}$
tracking resistance evaluation A (min)	$\geq 360$	$\geq 360$	$\geq 360$
evaluation B (min)	$\geq 360$	$\geq 360$	$\geq 360$
<u>after dipping in water for 100 hours</u>			
volume resistivity ( $\Omega$ -cm)	$1.1 \times 10^{14}$	$9.5 \times 10^{13}$	$2.4 \times 10^{10}$
dielectric constant	4.8	4.5	7.8
dissipation factor	$2.2 \times 10^{-2}$	$1.5 \times 10^{-2}$	$2.5 \times 10^{-1}$
water absorption (%)	0.2	0.25	1.9



Table 2

	Example 3	Comparative Example 2
<u>initial</u>		
volume resistivity ( $\Omega$ -cm)	$1.9 \times 10^{14}$	$2.0 \times 10^{14}$
dielectric constant	4.4	4.2
dissipation factor	$1.1 \times 10^{-2}$	$2.0 \times 10^{-2}$
tracking resistance evaluation A (min)	$\geq 360$	$\geq 360$
evaluation B (min)	$\geq 360$	$\geq 360$
<u>after dipping in water for 100 hours</u>		
volume resistivity ( $\Omega$ -cm)	$7.0 \times 10^{13}$	$2.1 \times 10^{10}$
dielectric constant	4.7	7.4
dissipation factor	$3.3 \times 10^{-2}$	$2.08 \times 10^{-1}$
water absorption (%)	0.28	1.5

Table 3

	Example 4
<u>initial</u>	
volume resistivity ( $\Omega$ -cm)	$7.5 \times 10^{14}$
dielectric constant	3.5
dissipation factor	$9.3 \times 10^{-3}$
tracking resistance evaluation A (min)	$\geq 360$
evaluation B (min)	$\geq 360$
<u>after dipping in water for 100 hours</u>	
volume resistivity ( $\Omega$ -cm)	$2.2 \times 10^{14}$
dielectric constant	3.8
dissipation factor	$1.2 \times 10^{-2}$
water absorption (%)	0.15